CALCULATIONS OF THE DIPOLE MOMENTS OF TRI-SUBSTITUTED BENZENES.—1, 2, 3-, 1, 2, 4-AND 1, 3, 5-SUBSTITUTIONS

D. V. G. L. NARASIMHA RAO

PHYSICS DEPARTMENT, ANDHRA UNIVERSITY, WALTAIR

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ABSTRACT. The previous calculations of the author on the dipole moments of 1, 2, 4 tri-substituted benzenes are now extended to the other two—1, 2, 3 and 1, 3, 5 substitutions. The equations of Frank are used in computing the induced moments since the dielectric constant of the internuclear space is introduced directly in these equations to account for its effect on the induced moments. Previous calculations on 1, 2, 4 substitution are also revised. The equation are applied in the first instance to a few typical molecules for which observed moments are available in the literature. Agreement between the calculated and observed values is found to be satisfactory for a majority of cases investigated. The calculated values also compared well with those deduced empirically by a previous worker.

INTRODUCTION

A general method was given by the author (Nara$_{\text{Simh}}$a Rao, 1955) for calculating the dipole- moments of 1, 2, 4 tri-substituted benzenes assuming the group moments as may be obtained from the observations on the corresponding mono-substituted compounds. The equations of Smallwood Herzfeld (1930) were used in computing the mutual induction of the three primary dipoles on one another and also the moments induced in the -CH and -C–C bonds of the hydrocarbon residue by the primary dipoles. The effect of the dielectric constant of the internuclear space was not considered in these equations. To allow for this effect the author has applied a correction by multiplying the total induced moment by the factor $\epsilon+2/3\epsilon$ where ϵ is the dielectric constant of the internuclear space assumed as 2.40 following Le Fevre and Le Fevre (1937). It was found that improved values could be obtained for the calculated moments when this correction was applied.

The calculations are now extended to the other two substitutions also, 1, 2, 3, and 1, 3, 5. The field equations of Frank (1935) are used in computing the induced moments since the dielectric constant of the internuclear space is directly involved in these equations so that no correction need be applied at the end. The previous calculations on 1, 2, 4 substitution are also revised and presented in the following pages.

CALCULATIONS

1, 2, 3 *substitution.* Figure 1 represents the case of a 1, 2, 3 substituted compound. The appropriate angles and distances are shown in the figure. ξ_1, ξ_2 and ξ_3 are the X-components, η_1, η_2, and η_3 are the Y-components of m_{01},

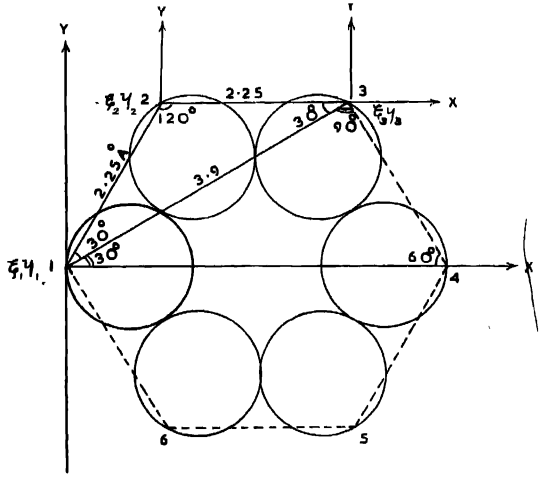

Fig. 1. 1 : 2 : 3 substitution.

m_{02} and m_{03} respectively (the actual group moment m_0 is given as $m_e = 1.843m_0$ where m_e is the moment of the mono-substituted compound). Applying the equations of Frank, the interaction of the three primary dipoles gives the follow-equations :

$$\begin{aligned}
&\xi'_1 + 0.1528a_1\xi'_2 - 0.7939a_1\eta'_2 - 0.7640a_2\xi'_3 - 0.7939a_2\eta'_3 = \xi_1\\
&\eta'_1 - 0.7939a_1\xi'_2 - 0.7640a_1\eta'_2 - 0.7939a_2\xi'_3 + 0.1528a_2\eta'_3 = \eta_1\\
&0.1528b_1\xi'_1 - 0.7939b_1\eta'_1 + \xi'_2 - 1.2224b_1\xi'_3 = \xi_2\\
&0.7939b_1\xi'_1 + 0.7640b_1\eta'_1 - \eta'_2 - 0.6112b_1\eta'_3 = -\eta_2\\
&0.7640c_2\xi'_1 + 0.7939c_2\eta'_1 + 1.2224c_1\xi'_2 - \xi'_3 = -\xi_3\\
&-0.7939c_2\xi'_1 + 0.1528c_2\eta'_1 + 0.6112c_1\eta'_2 + \eta'_3 = \eta_3 \qquad \ldots (1)
\end{aligned}$$

where
$$\begin{aligned}
&\alpha_1/r^3_1 = a_1. \quad \alpha_1/r^3_2 = a_2, \quad \alpha_1/r^3_3 = a_3\\
&\alpha_2/r^3_1 = b_1, \quad \alpha_2/r^3_2 = b_2, \quad \alpha_2/r^3_3 = b_3\\
&\alpha_3/r^3_1 = c_1, \quad \alpha_3/r^3_2 = c_2, \quad \alpha_3/r^3_3 = c_3. \qquad \ldots (2)
\end{aligned}$$

α_1, α_2, α_3 are the polarisabilities of the three substituent groups. In setting up these equations the fields of the induced moments are also considered since we have written $\xi' = \xi + \xi_i$ and $\eta' = \eta + \eta_i$. Thus as a result of dipolar induction

each ξ is modified to a certain ξ' and each η to a certain η'. In order to obtain the numerical values of ξ' and η', the six equations (1) are solved by the method of post-multiplication (Frazer, Duncan and Collar-1938) giving the values of the six variables.

The induced moments in the remaining $-$CH groups at 4, 5, 6 positions are calculated along similar lines. Values of the necessary angles and distances are given in Table I below.

TABLE I

Group		(4)	(5)	(6)	
1	r	4.5	3.9	2.25	Å
	v	0°	−30°	−60°	
2	r	3.9	4.5	3 9	
	v	−30°	60°	−90°	
3	r	2.25	3.9	4 5	
	x	−60°	−90°	−120°	

The final values are given as

$$\Sigma\xi_i = 0.008424\xi'_1 - 0.0543\eta'_1 + 0.0005861\xi'_2 - 0.01445\eta'_2 - 0.01663\xi'_3 - 0.03985\eta'_3$$
$$\Sigma\eta_i = -0.05433\xi'_1 + 0.03780\eta'_1 - 0.01445\xi'_2 + 0.01728\eta'_2 - 0.03985\xi'_3 + 0.06284\eta'_3 \quad \ldots (3)$$

In evaluating the induced moments in the –C–C bonds the various angles and distances are shown in Table II.

TABLE II

Group		(1)	(2)	(3)	(4)	(5)	(6)
1	r	1.3	2.6	3.438	3.438	2.6	1.3Å
	v	30°	30°	10°54′	−10°54′	−30°	−30°
2	r	1.3	2.6	3.438	3.438	2.6	1 3
	v	−30°	−30°	−49°6′	−70°54′	−90°	−90°
3	r	1 3	2.6	3.438	3.438	2 6	1.3
	v	−90°	−90°	−109°6′	−130°54′	−150°	−150°

The sum of the induced moments in –C–C bonds is given as

$$\Sigma\xi'_i = 0.8265\xi'_1 + 0.07124\xi'_2 - 0.4359\eta'_2 + 0.07124\xi'_3 + 0.4359\eta'_3$$
$$\Sigma\eta'_i = -0.1806\eta'_1 - 0.4359\xi'_2 + 0.5746\eta'_2 + 0.4359\xi'_3 + 0.5746\eta'_3 \quad \ldots (4)$$

The total contribution due to induction in the unsubstituted —C—H groups and in the —C—C bonds is obtained as

$$\Sigma(\xi_i+\xi'_i) = 0.8349\xi'_1-0.05433\eta'_1+0.7183\xi'_2-0.4504\eta'_2+0.05461\xi'_3+0.3961\eta'_3$$
$$\Sigma(\eta_i+\eta'_i) = -0.05433\xi'_1-0.1427\eta'_1-0.4504\xi'_2+0.5919\eta'_2+0.3961\xi'_3+0.6374\eta'_3 \quad \ldots (5)$$

Finally the resultant moment of the molecule is given as

$$\mu = (M^2_x + M^2_y)^{\frac{1}{2}}$$

where $M_x = \Sigma(\xi_i + \xi'_i) + \xi'_1 + \xi'_2 + \xi'_3$

$$= 1.8349\xi'_1-0.05433\eta'_1+1.07183\xi'_2-0.4504\eta'_2+1.05461\xi'_3+0.3961\eta'_3$$

$$M_y = \Sigma(\eta_i+\eta'_i)+\eta'_1+\eta'_2+\eta'_3$$
$$= -0.05433\xi'_1+0.8573\eta'_1-0.4504\xi'_2+1.5919\eta'_2+0.3961\xi'_3+1.6374\eta'_3 \quad (6)$$

1 : 2 : 4 *Substitution.* Figure 2 gives a picture of this type of compound. A consideration of the interaction of the three primary dipoles gives the relations

$$\xi'_1+0.1528a_1\xi'_2-0.7939a_1\eta'_2-1.2224a_3\xi'_3=\xi_1$$

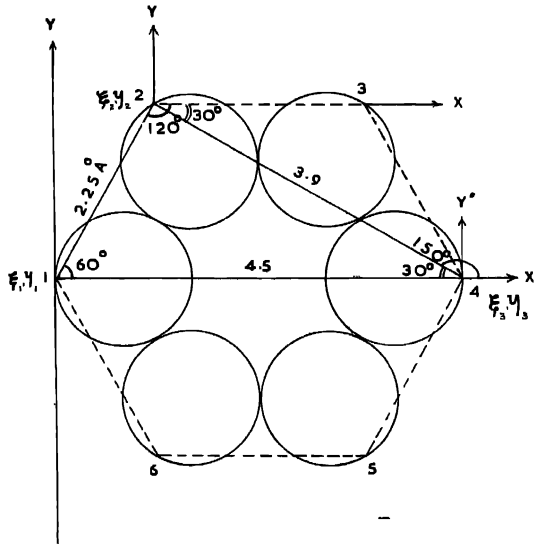

Fig. 2. 1 : 2 : 4 substitution

$$\eta'_1-0.7939a_1\xi'_2-0.7640a_1\eta'_2+0.6112a_3\eta'_3=\eta_1$$
$$0.1528b_1\xi'_1-0.7939b_1\eta'_1+\xi'_2-0.7640b_2\xi'_3+0.7939b_2\eta'_3=\xi_2$$
$$-0.7939b_1\xi'_1-0.7640b_1\eta'_1+\eta'_2+0.7939b_2\xi'_3+0.1528b_2\eta'_3=\eta_2$$

$$-1.2224c_2\xi'_1-0.7640c_2\xi'_2+0.7939c_2\eta'_2+\xi'_3=\xi_3$$
$$0.6112c_2\eta'_1+0.7939c_2\xi'_2+0.1528c_2\eta'_2+\eta'_3=\eta_3 \quad \ldots (7)$$

In this case the sum of the contributions of the induced moment in the unsubstituted —C—H and —C—C bonds (the necessary distances and angles are given in Tables I and II of the previous paper—Narasinha Rao 1955) is

$$\Sigma(\xi_i+\xi_i') = 0.8343'\xi_1+0.04558\eta'_1+0.1337\xi'_2-0.4416\eta'_2+0.8149\xi'_3+0.008752\eta'_3$$
$$\Sigma(\eta_i+\eta'_i)=-0.04558\xi'_1-0.1400\eta'_1-0.4416\xi'_2+0.5584\eta'_2+0.008752\xi'_3-$$
$$0.09450\eta'_3 \quad \ldots (8)$$

The resultant moment is again

$$\mu = (M_x^2+M_y^2)^{\frac{1}{2}}$$

with $M_x = 1.8343\xi'_1+0.04558\eta'_1+1.1337\xi'_2-0.4416\eta'_2+1.8149\xi'_3+0.008752\eta'_3$
$M_y=-0.04558\xi'_1+0.8600\eta'_1-0.4416\xi'_2+1.5584\eta'_2+0.008752\xi'_3+0.9055\eta'_3$
$\ldots (9)$

1, 3, 5 *substitution.* The method of calculation may be understood from figure 3. The induced effects in the primary dipoles give the following equations.

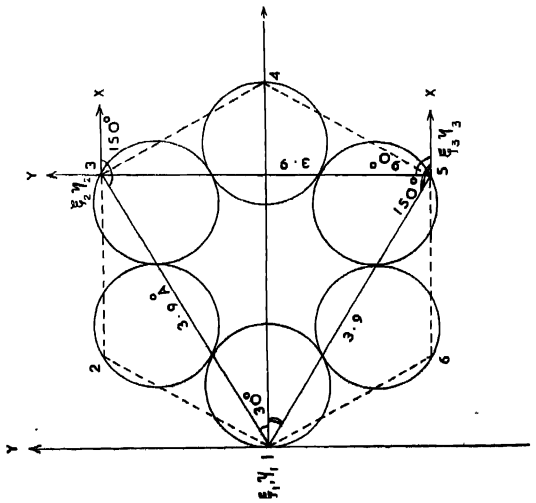

Fig. 3. 1 3 : 5 substitution

$$\xi'_1-0.7640a_2\xi'_2-0.7939a_2\eta'_2-0.7640a_2\xi'_3+0.7939a_2\eta'_3=\xi_1$$
$$\eta'_1-0.7939a_2\xi'_2+0.1528a_2\eta'_2+0.7939a_2\xi'_3+0.1528a_2\eta'_3=\eta_1$$

$$-0.7640b_2\xi'_1-0.7939b_2\eta'_1+\xi'_2+0.6112b_2\xi'_3=\xi_2$$
$$-0.7939b_2\xi'_1+0.1528b_2\eta'_1+\eta'_2-1.2224b_2\eta'_3=\eta_2$$
$$-0.7640c_2\xi'_1+0.7939c_2\eta'_1+0.6112c_2\xi'_2+\xi'_3=\xi_3$$
$$0.7939c_2\xi'_1+0.1528c_2\eta'_1-1.2224c_2\eta'_2+\eta'_3=\eta_3 \qquad \ldots \quad (10)$$

In computing the induced moments in the unsubstituted –C–H groups and –C–C bonds the angles and distances are given in Tables III and IV respectively.

TABLE III

Group		(2)	(4)	(6)
1	r	2.25	4.5	2.25Å
	x	60°	0°	−60°
2	r	2.25	2.25	4.5
		180°	−60°	−120°
3	r	4.5	2.25	2.25
	v	120°	60°	180°

TABLE IV

Group		(1)	(2)	(3)	(4)	(5)	(6)
1	r	1.3	2.6	3.438	3.438	2.6	1.3Å
	v	30°	30°	10°54′	−10°54′	−30°	−30°
2	r	1.3	2.6	3.438	3.438	2.6	1.3
	v	−90°	−90°	−109°6′	−130°54′	−150°	−150°
3	r	1.3	2.6	3.438	3.438	2.6	1.3
	v	150°	150°	130°54′	109°6′	90°	90°

For this substitution

$$\Sigma(\xi_i+\xi'_i) = 0.8179\xi'_1+0.1315\xi'_2+0.3961\eta'_2+0.1315\xi'_3-0.3961\eta'_3$$
$$\Sigma(\eta_i+\eta'_i) = -0.1361\eta'_1+0.3961\xi'_2+0.5887\eta'_2-0.3961\xi'_3+0.5887\eta'_3 \qquad \ldots \quad (11)$$

Finally the total moment of the molecule is given as

$$\mu = (M_x^2+M_y^2)^{\frac{1}{2}} \qquad \text{with}$$

$$M_x = 1.8179\xi'_1+1.1315\xi'_2+0.3961\eta'_2+1.1315\xi'_3-0.3961\eta'_3$$
$$M_y = 0.8634\eta'_1+0.3961\xi'_2+1.5887\eta'_2-0.3961\xi'_3+1.5887\eta'_3 \qquad \ldots \quad (12)$$

RESULTS AND DISCUSSION

The method described above is applied to specific cases in the first instance to a few typical molecules for which the observed values are obtained from the compilation of Wesson (1948) and listed in the following Table V. The deviations

$\Delta = \mu_{obs.} \sim \mu_{calcd.}$ and $\delta = \mu_{obs.} \sim \mu_{vector}$ are also given in the table for comparison. A particular point to be noted is the choice of the moment m_e of the mono-substituted benzene to be used in the calculation, since for the same molecule various values have been reported in the literature. Values of m_e considered to be the most probable by the author and hence used throughout are given in Table VI.

TABLE V

Compound	$\mu_{obs.}$	$\mu_{calcd.}$	μ_{vector}	Δ	δ
2, 3-Dichloronitrobenzene	3.86	4.34D	4.78	0 48	0.92
2, 4-Dichloronitrobenzene	2.66	3.01	3 45	0.35	0.79
2, 5-Dichloronitrobenzene	3 45	3.64	3 95	0 19	0.50
2, 6-Dichloronitrobenzene	4.18	4.76	5 50	0.58	1 32
3, 5-Dichloronitrobenzene	2 66	2.49	2.40	0.17	0.26
1, 3-5, Trichlorobenzene	0.28	0.00	0.00	0 28	0.28
1, 3-5, Triiodobenzene	0 24	0.00	0.00	0.24	0.24
3, 5-Dinitrotoluene	4 05	4.16	4.34	0 11	0 29

TABLE VI

Group	m_g
NO_2	−3.95
Cl	−1.55
I	−1.25
CH_3	+0.39
NH_2	+1.53

Conventionally the group moment is considered positive when the dipole moment vector of the group is directed towards the centre of the benzene ring and negative when it is directed away from the centre. The polarisability values α of the various groups are assumed from Smallwood and Herzfeld's results (1930). Judged from the magnitudes of Δ and δ in Table V it may be seen that for all the molecules studied the calculated moments are nearer the observed values when the induced moments are taken into account. For the two symmetric substitutions, 1, 3, 5 tri-chloro- and 1, 3, 5 tri-iodo benzenes, the induced moments get cancelled and the author's detailed calculation also gives a zero moment. The reported

values may be due perhaps to the neglect of atom polarisation as in the similar case sym- tri-nitrobenzene.

The first five molecules listed in the table are the subject of investigation by Thomson (1944)—a sixth isomer is also studied by him— to ascertain whether there is any steric inhibition of resonance of the nitro group due to vicinal Cl groups. The molecular solution volumes and molecular refractivities support the view that in 2, 6-dichloronitrobenzene where there are two Cl groups ortho to NO_2 group, resonance between the NO_2 group and benzene ring is to a large extent inhibited. It is suggested that even one Cl ortho to NO_2 will have a certain inhibitory effect on the resonance. Variations in the parachors are of the same magnitude and sign as variations in molecular solution volumes. It may hence be expected that the dipole moment of 2, 6-dichloronitrobenzene will be lower than the calculated value even after allowance for inductive effects. He points out that values found for dipole moments "are not inconsistent with this view". Calculated moments are obtained by Thomson using certain empirical rules regarding the interaction of Cl and NO_2 groups. (a) Each chlorine ortho to a nitro group will result in a diminution of moment of 0.59D. This correction includes at least two factors- the effect of induction and the effect of inhibition of resonance. (b) A chlorine meta to a nitro- group will result in an increase of moment by 0.15. In his calculations the assumed values of moments are $C_6H_5NO_2$—3.97, *o*-$C_6H_4Cl_2$—2.25, *m*-$C_6H_4Cl_2$—1.48, *p*-$C_6H_4Cl_2$. A comparison is made between the values calculated by the author and those of Thomson in Table VII below.

TABLE VII

Compound	(Thomson) $\mu_{calcd.}$	(author) $\mu_{calcd.}$	Δ
2, 3-Dichloronitrobenzene	3.97	4.34	0.37
2, 4-Dichloronitrobenzene	3.03	3.01	0.02
2, 5-Dichloronitrobenzene	3.38	3.64	0.26
2, 6-Dichloronitrobenzene	4.27	4.76	0.49
3, 5-Dichloronitrobenzene	2.49	2.49	0.00

The difference between the two types of calculation is shown under Δ' in the table. Δ' may be taken as an extent of the inhibition of resonance, since a correction for this effect is applied by Thomson inherent in rule (ā) whereas the author's values take account of induction only. There is no method at present to make an exact estimate of this effect by simple theory. As a logical consequence of the arguments of Thomson, we may expect that in 2 : 6 dichloronitrobenzene in which the proposed effect must be most pronounced, the nitro-group moment may have approximately the same value as the corresponding aliphatic compound.

nitromethane. If now the calculations are repeated using this value for m_e the observed moment may be explained. Such a procedure has been worked out assuming $m_e = 3.10$D and as per our predictions the calculated moment turns out as 3.94 D which is slightly less than the observed value 4.18 indicating that resonance of the NO_2 group is inhibited to a large extent, thus establishing the essential point of Thomson.

In 3, 5-dinitro-toluene no such complications are expected since there are no methyl or Cl groups ortho to the NO_2 group and as expected the agreement between calculated and observed values is within experimental error.

A critical account of the assumptions made in the procedure worked out for calculating the induced moments and their validity has been given in the previous paper by the author.

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